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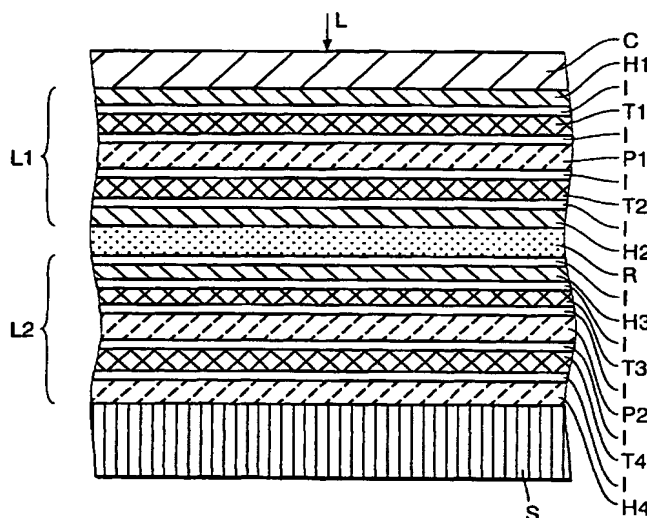
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[Continued on next page]

(54) Title: MULTI-STACK OPTICAL INFORMATION CARRIER COMPRISING THERMOCHROMIC LAYER



(57) Abstract: The present invention relates to a multi-stack optical information carrier for recording information by means of a laser beam, said optical information carrier comprising: - a substrate layer (S), - at least two recording stacks (L1, L2), each comprising a recording layer (P1, P2), at least one heat sink layer (H1-H4) and dielectric layers (I) between said recording layer (P1, P2) and said at least one heat sink layer (H1-H4), - at least one spacer layer (R) separating the at least two recording stacks (L1, L2), and - a cover layer (C). In order to improve the sensitivity during writing, preferably in the first recording stack (L1), it is proposed according to the present invention that at least one recording stack (L1, L2) further comprises at least one thermochromic layer (T1, T2, T3) having temperature-dependent optical characteristics for improving the sensitivity of at least one of said recording stacks (L1) during recording.

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## Multi-stack optical information carrier comprising thermochromic layer

The present invention relates to a multi-stack optical information carrier for recording information by means of a laser beam, said optical information carrier comprising

- a substrate layer,
- at least two recording stacks, each comprising a recording layer, at least one
- 5 heat sink layer and dielectric layers between said recording layer and said at least one heat sink layer,
- at least one spacer layer separating the at least two recording stacks,
- a cover layer.

10

Such multi-stack optical information carriers are known, for instance from US 6,190,750. Such optical information carriers are applied as recordable (write once) or rewritable (write multiple times) information carriers in DVD or DVR technology, for instance as dual layer disc comprising two layers of a phase-change material. Optical

15 information carriers can also have more than two recording layers, i.e. several recording stacks on top of each other, and other recording materials than phase-change material.

In such optical information carriers the recording layers are made of phase-change material, such as chalcogenide alloys, Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> alloys, SbTe alloys, etc. Further useful alloys are In-Sb-Te, Te-Se-Te, Ag-In-Sb-Te, Ge-In-Sb-Te or Ge-Te. Especially useful

20 compounds are described in the patent application WO 01/13370 and WO 97/50084. Said materials are characterized in that the said phase-change material can have a crystalline and an amorphous phase. The amorphous phase is obtained by locally heating said initially crystalline recording layer with a focussed laser beam to above its melting temperature, and subsequent quenching (fast cooling) it. The crystalline phase is obtained by heating the

25 amorphous material with focussed laser spot to above the glass transition temperature to allow re-crystallization of the phase-change material. These phase changes are reversible making this material suitable for multiple write cycles. Also one write cycle is possible. By applying a sequence of laser pulses with high (writing) and lower (erasing) laser power, an alternating sequence of amorphous marks and crystalline spaces is obtained that represent the

binary data. The different optical properties of the amorphous and the crystalline phase allow read out of data. This type of phase-change material can also be applied in write once discs. The initial state of the phase-change material may be as-deposited amorphous or crystalline, the phase of the written mark being its counterpart. This means that amorphous marks may be written by melt-quenching the phase-change layer. Crystalline marks may be written by crystallization of the initially amorphous material.

In a dual-stack information carrier, both information (recording) layers are written and read by the same optical laser beam. To optically access the deep recording stack, the first recording stack needs to be semitransparent. To be able to write data in the deep recording stack, the first recording stack needs about 50% transparency. If the reflection of the first recording stack is 10%, about 40% absorption of the incident light remains. A transmission of 50% is achieved only if thick metallic heat sink layers are omitted from the recording stacks. These thick metallic layers are typically used in conventional phase-change recording stacks. The omission of a thick metallic heat sink layer leads to slow-cooling behavior. The thermal response may be improved by the addition of thin metallic layers, such as 10 nm Ag layers, or semitransparent heat sink layers. While the cooling rate is significantly improved by the addition of these semitransparent heat sink layers, the absorption is still 40%. As a consequence much more laser power is required to melt-quench the phase-change layer for writing amorphous marks in the crystalline layer. Typically, twice the write power is needed when semitransparent heat sink layers are applied with a thermal conductivity of about 5 times that of ZnS-SiO<sub>2</sub>, as typically used in single-stack phase-change discs.

It is therefore an object of the present invention to provide a multi-stack optical information carrier having an improved sensitivity during writing, in particular in the first recording stack.

This object is achieved according to the present invention by an information carrier as claimed in claim 1, which is characterized in that at least one recording stack further comprises at least one thermochromic layer having temperature-dependent optical characteristics for improving the sensitivity of at least one of said recording stacks during recording.

The invention is based on the idea that the presence of a thermochromic layer is only sensed when data are written in the first recording stack, i.e. the laser beam is

focussed on said phase-change recording stack. More precisely, a dual-stack optical recording carrier shall be considered as an example, which comprises two recording stacks that are separated by a spacer layer of about 10-100 $\mu$ m thickness (the lower values refer to high density information carriers, such as BD (former DVR system), the higher values refer to for example DVD dual-stack discs). In one state, when the incident laser beam is focussed on the deep recording stack, the first recording stack experiences a defocused laser beam. Although the absorption of the first recording stack is still 40%, the optical energy is spread out across a very large area. The optical energy density is such low that the first recording stack is not effectively heated up. In this situation, the additional thermochromic layer remains at low temperature and the optical properties of said thermochromic layer are not noticeably changed.

In the other state, when the laser beam is focussed on the first recording layer, the optical energy density is much higher due to the diffraction limited optical spot. The absorbed laser power, 40% of the incident light, is now concentrated in a very small area such that the corresponding temperature rise amounts easily the melting temperature of the phase-change material. If a thermochromic layer is located in the vicinity of the phase-change layer, said thermochromic layer will also experience a significant temperature rise (100-200C). This temperature rise is sufficient to allow a significant change of the optical properties of the said thermochromic layer. This results in either an increased reflection or increased absorption of the thermochromic layer. An increased absorption leads to an increased temperature. In this way, a self-strengthening effect is achieved being that more laser power is effectively used to heat up the first recording stack to enable writing and erasing of data.

Preferred embodiments of the multi-stack optical information carrier are defined in the dependent claims. In a first embodiment the thermochromic layers have a temperature-dependent absorption characteristic in which case preferably a thermochromic dye material, in particular cyanine or phthalocyanine dye, is used as material. According to an alternative embodiment the thermochromic layers have a temperature dependent reflection characteristic, in which case preferably vanadium dioxide is used as material.

A further improvement of the sensitivity during writing can be achieved by an embodiment in which each recording stack comprises at least one thermochromic layer. Moreover, in another embodiment at least one recording stack comprises at least two thermochromic layers, i.e. one thermochromic layer on each side of the recording layer

separated there from it by a dielectric layer. Thus, even each recording stack may comprise two thermochromic layers arranged in this way.

5           The invention will now be explained in more detail with reference to the drawings in which:

Fig. 1 diagrammatically shows a cross-section of a first embodiment of an optical information carrier according to the present invention,

10           Fig. 2 diagrammatically shows a cross-section of another embodiment of an optical information carrier according to the present invention,

Fig. 3 shows the reflection during and after DC-write as a function of the DC power for two recording speeds,

Fig. 4 shows the reflection of phthalocyanine dye as a function of the temperature, and

15           Fig. 5 shows the temperature-dependent reflection of IPI-dye stacks.

Fig. 1 diagrammatically shows a cross section of a first embodiment of a dual-layer information carrier according to the present invention. Shown are, from top, where the laser light L is incident, to bottom:

- a cover layer C for protection,
- a first transparent heat sink layer H1, for example made of indium-tin-oxide (ITO), aluminum nitride (AlN) or hafnium nitride (HfN),
- a dielectric layer I as interference layer, e.g. made of  $Ta_2O_5$ ,  $ZnS-SiO_2$ ,  $TiO_2$ ,
- 25 - a first thermochromic layer T1 as absorption layer, for example made of a thermochromic dye,
- a dielectric layer I,
- a first phase-change recording layer P1, e.g. made of  $Ge_2Sb_2Te_5$  or doped SbTe,
- 30 - a dielectric layer I,
- a second thermochromic layer T2,
- a dielectric layer I,
- a second heat sink layer H2,

- a spacer layer R to optically and thermally separate the two recording stacks (10-100 $\mu$ m)

- a dielectric layer I

- a third heat sink layer H3

5 - a dielectric layer I

- a third thermochromic layer T3

- a dielectric layer I

- a second phase change recording layer P2,

- a dielectric layer I,

10 - a forth thermochromic layer T4 as absorption layer,

- a dielectric layer I,

- a forth heat sink layer H4, which must not be semi-transparent, but can be made of a metal, e.g. Ag, Al, and

- a substrate S, e.g. of polycarbonate.

15 As explained above when the laser beam L is focussed on the second recording stack L2 still 50% of the incident laser power is available for writing in the lower L2 stack since at temperatures up to about 100°C the thermochromic layers T1, T2 have a sufficiently high transmission rate. However, when the laser beam L is focussed on the upper recording stack L1, the stack L1 including the additional thermochromic layers T1 and T2  
20 heats up. This involves a significant change of the optical properties of the thermochromic layer and leads to an increased absorption of stack L1 due to an increased reflection or absorption of the thermochromic layers T1, T2. Thus, more laser power is effectively used to heat up the first recording layer P1 and provides a self-strengthening effect.

The thickness of the dielectric layer I between the phase change layer P1 and  
25 the thermochromic layer T1 and T2 can be chosen such that the temperature drop across these layers results in the optimum temperature rise of T1 and T2 such that optimum absorption results (i.e. the temperature should not exceed 250°C to prevent decomposition of the thermochromic layer). For the write-once variant of this invention, this decomposition is not an issue and these higher temperatures are thus allowed. Further, the other layers in the  
30 stack contribute to the thermal response of the entire stack as well and, therefore, their thickness and thermal properties (read material) should be selected carefully to ensure an optimum temperature rise of the thermochromic layers.

The described embodiment can be modified by e.g. only providing the upper recording stack L1 with one or two additional thermochromic layers as shown, but not the

lower recording stack L2. Further, more than two recording stacks can be provided. Still further, the dielectric layers I provided on each side of the recording layers P1, P2 can also be omitted.

Another embodiment of an optical information carrier according to the present invention is diagrammatically shown as a cross-section in Fig. 2. Therein, again two recording stacks L1, L2 are provided, each comprising one additional thermochromic layer T1 or T2, respectively. In this embodiment, the thermochromic layers T1, T2 are adapted such that they show a temperature-dependent reflection characteristic, i.e. the reflection rate of the thermochromic layers T1, T2 increases with temperature. Preferably, vanadium dioxide VO<sub>2</sub> is used as material for such thermochromic layers.

The temperature-dependent absorption of two types of discs (CD-R) was investigated, namely cyanine and phthalocyanine dyes. The temperature-dependent absorption of a phthalocyanine dye is illustrated in Fig. 3. The reflection during DC-write and after DC-write is given as a function of the applied continuous write power. A clear power range is observed in which the reflection drops reversibly. This indicates that during writing, at an elevated temperature, the absorption of the stack was significantly increased but that after passage of the laser spot, after cooling down of the stack, that the reflection remained its initial value (at room temperature).

The reflection change as a function of temperature was also measured for a phthalocyanine dye, see Fig. 4. The experiments have been performed in an N<sub>2</sub> and O<sub>2</sub> environment. Two phenomena are clearly observable. The gradual reversible decrease in reflection is attributed to the increased absorption with increasing temperature. Further, the irreversible degradation of the dye around 275°C.

Both results illustrate that the absorption of the dye is temperature-dependent. If a dye layer is used in an IPI phase-change stack, leading to an IPI-dye stack, the dye layer starts to absorb laser light at elevated temperature. To prevent degradation of the dye layer, for application in a rewritable format, the dielectric layer between the recording layer (P) and thermochromic dye layer (T) should preferably be between 10-200 nm, in particular between 30-100 nm.

In the other embodiment, it is proposed to use a dye layer as a thermochromic reflector: at elevated temperatures, the index of refraction is changed leading to an increased absorption in the recording layer. Optical calculations prove this.

It is also possible to apply an additional dye layer to a write-once PC-disc: a multi-stack disc: IPI-dye – spacer – IPI-dye – etc. or dye-IPI-dye – spacer – dye-IPI-dye – spacer etc.

5 The dielectric layer between the recording and dye layer is preferably between 0 and 50 nm, degradation of the dye is then allowable.

Fig. 5 shows the temperature-dependent reflection of IPI-dye stacks, measured during heating up and cooling down of the recording stacks. The reversible change in optical properties of the stack, caused by the thermochromic layer, is clearly observed from the measurements. Shown are measurements of the normalized reflection 1 and of the  
10 normalized transmission 2.

## CLAIMS:

1. A multi-stack optical information carrier for recording information by means of a laser beam, said optical information carrier comprising:

- a substrate layer,
- at least two recording stacks, each comprising a recording layer, at least one
- 5 heat sink layer and dielectric layers between said recording layer and said at least one heat sink layer,
- at least one spacer layer separating the at least two recording stacks, and
- a cover layer,

10 characterized in that at least one recording stack further comprises at least one thermochromic layer having temperature-dependent optical characteristics for improving the sensitivity of at least one of said recording stacks during recording.

2. A multi-stack optical information carrier as claimed in claim 1, characterized in that said at least one thermochromic layer has a temperature-dependent absorption

15 characteristic.

3. A multi-stack optical information carrier as claimed in claim 2, characterized in that said thermochromic layer is essentially made of a thermochromic dye, in particular cyanine or phthalocyanine dye.

20

4. A multi-stack optical information carrier as claimed in claim 1, characterized in that said at least one thermochromic layer has a temperature-dependent reflection characteristic.

25 5. A multi-stack optical information carrier as claimed in claim 4, characterized in that said thermochromic layer is essentially made of vanadium dioxide.

6. A multi-stack optical information carrier as claimed in claim 1, characterized in that each recording stack comprises at least one thermochromic layer.

7. A multi-stack optical information carrier as claimed in claim 1, characterized in that at least one recording stack comprises a thermochromic layer on both sides of the recording layer and dielectric layers for separating the thermochromic layers from the recording layer.
- 5
8. A multi-stack optical information carrier as claimed in claim 1, characterized in that said recording layers are made of a phase-change material.
- 10 9. A multi-stack optical information carrier as claimed in claim 1, characterized in that said recording layers are made of a write-once material.

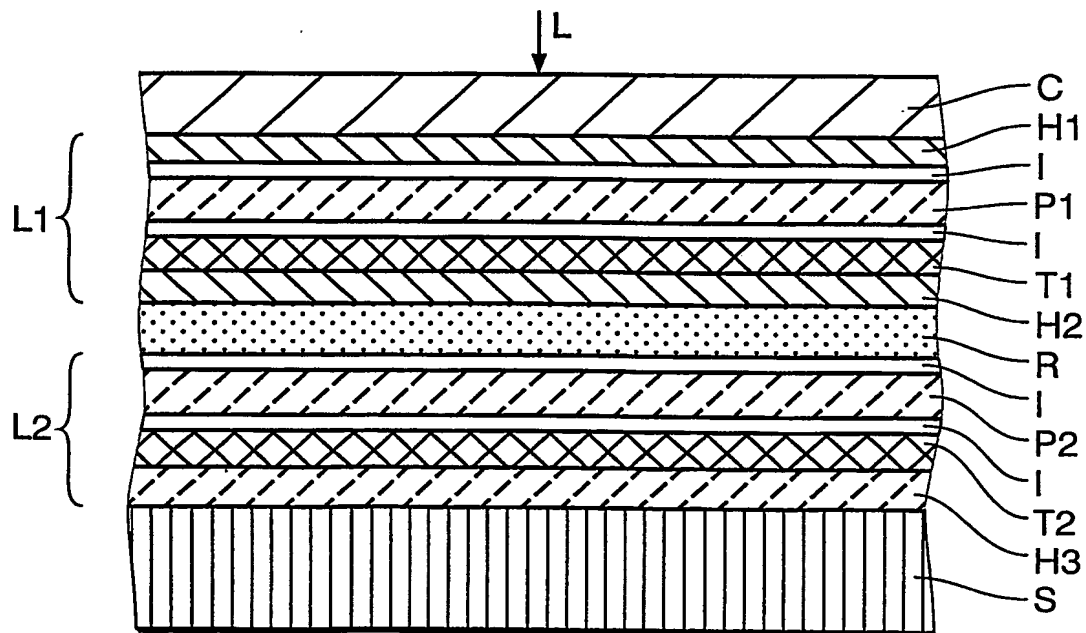
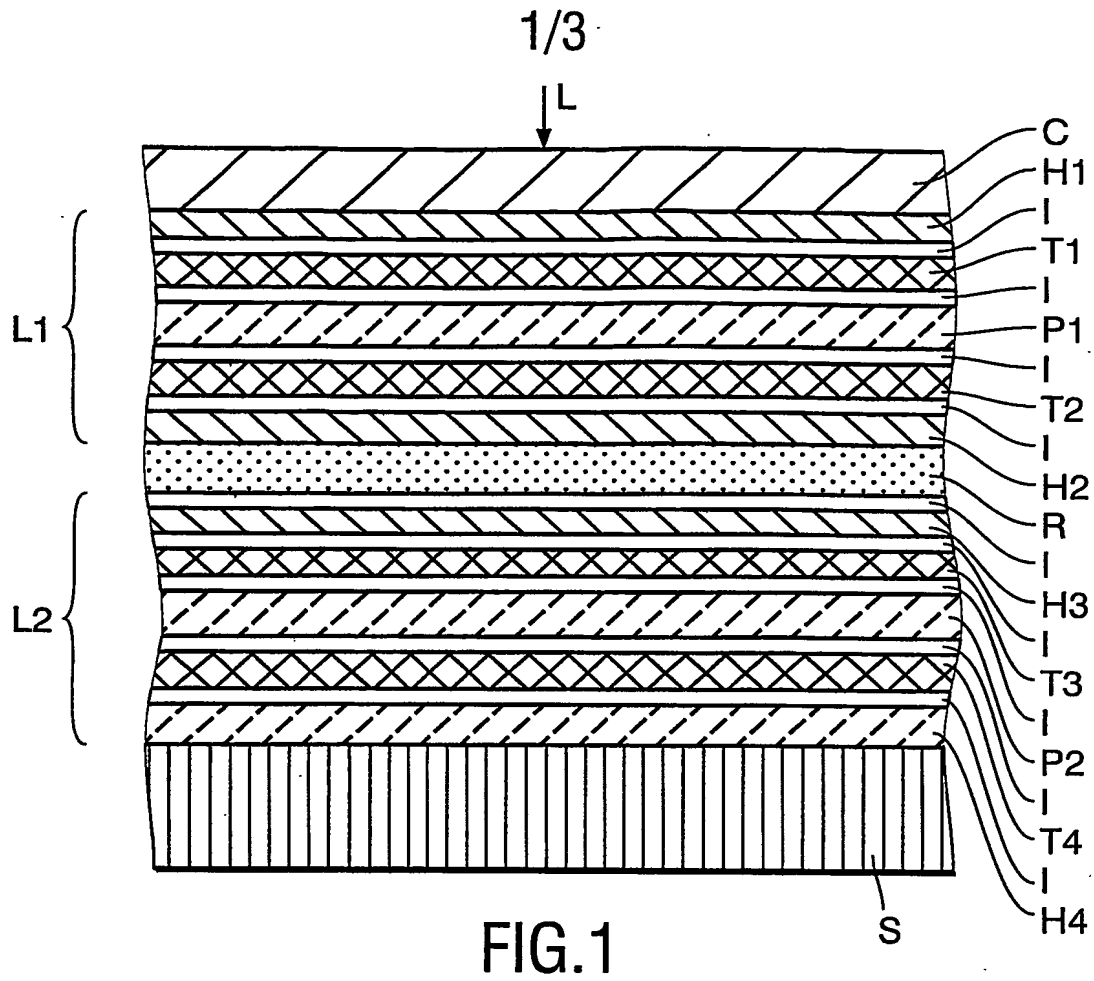


FIG.2

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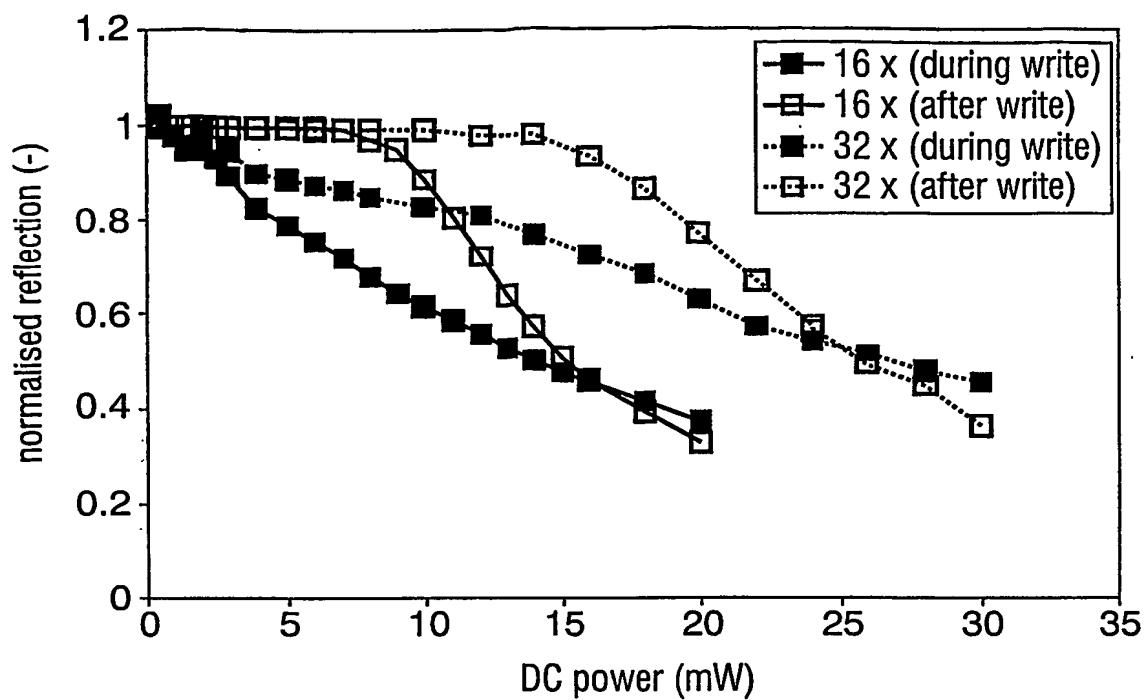


FIG. 3

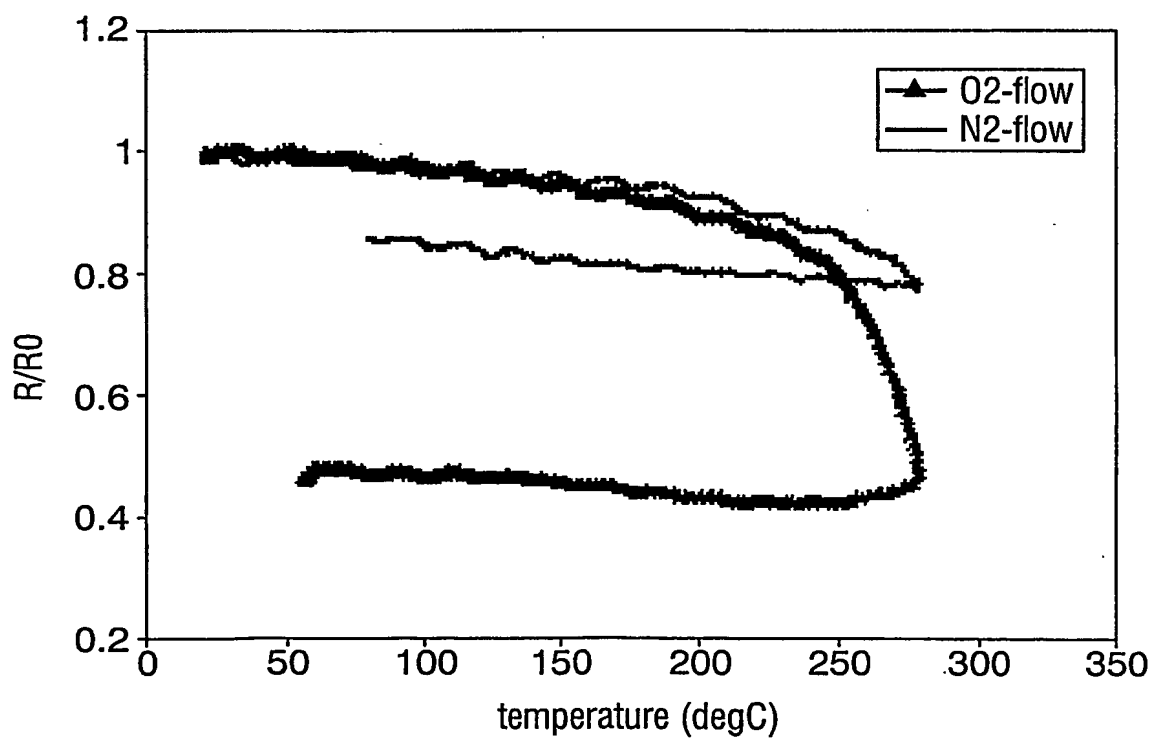


FIG. 4

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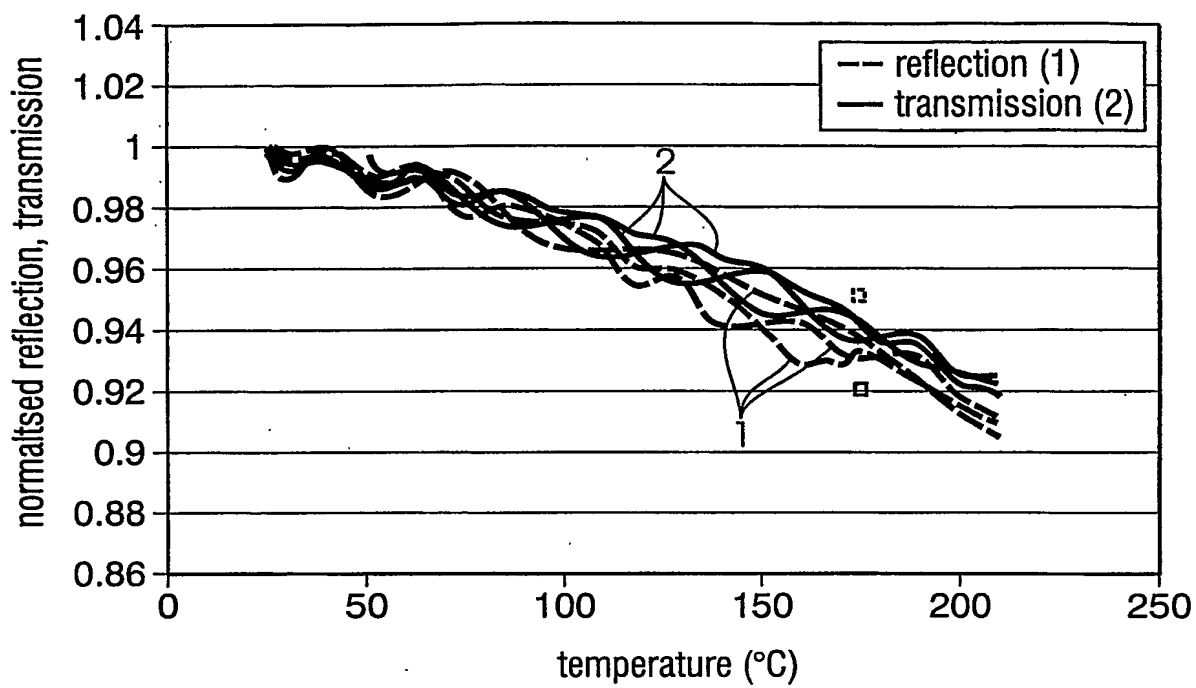


FIG.5

## INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 G11B7/24

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 G11B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No. |
|------------|---|-----------------------|
| X          | US 6 231 945 B1 (M MIYAMOTO)<br>15 May 2001 (2001-05-15)<br>column 2, line 4 -column 6, line 29;<br>claims 1-27; figure 1<br>column 3, line 61<br>column 4, line 50 | 1,5                   |
| Y          | US 2002/018870 A1 (E R MEINDERS)<br>14 February 2002 (2002-02-14)<br>column 2, paragraph 19; claims 1-7; figure 1   | 1,3                   |
| Y          | US 2001/016242 A1 (M MIYAMOTO)<br>23 August 2001 (2001-08-23)<br>column 4, paragraph 58 - paragraph 61;<br>claims 1-6; figure 1                                     | 1,3                   |
|            | ---<br>-/--   |                       |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages   | Relevant to claim No. |
|------------|--|-----------------------|
| Y          | US 5 297 132 A (A TAKANO)<br>22 March 1994 (1994-03-22)<br>column 5, line 1 - line 20; claims 1-6;<br>examples I-2<br>column 5, line 61<br>----- | 1,3                   |

## INTERNATIONAL SEARCH REPORT

PCT/03/02848

| Patent document<br>cited in search report |    | Publication<br>date |    | Patent family<br>member(s) | Publication<br>date |
|---|----|---------------------|----|----------------------------|---------------------|
| US 6231945                                | B1 | 15-05-2001          | WO | 9913465 A1                 | 18-03-1999          |
|   |    |                     | US | 2001023006 A1              | 20-09-2001          |
| US 2002018870                             | A1 | 14-02-2002          | CN | 1388962 T                  | 01-01-2003          |
|   |    |                     | WO | 0205274 A1                 | 17-01-2002          |
|   |    |                     | EP | 1208565 A1                 | 29-05-2002          |
|   |    |                     | TW | 508573 B                   | 01-11-2002          |
| US 2001016242                             | A1 | 23-08-2001          | JP | 2001209974 A               | 03-08-2001          |
|   |    |                     | TW | 484134 B                   | 21-04-2002          |
| US 5297132                                | A  | 22-03-1994          | JP | 2588524 B2                 | 05-03-1997          |
|   |    |                     | JP | 63237993 A                 | 04-10-1988          |
|   |    |                     | JP | 63111093 A                 | 16-05-1988          |
|   |    |                     | JP | 63135292 A                 | 07-06-1988          |
|   |    |                     | JP | 2521069 B2                 | 31-07-1996          |
|   |    |                     | JP | 63137893 A                 | 09-06-1988          |
|   |    |                     | JP | 63145086 A                 | 17-06-1988          |
|   |    |                     | AU | 612602 B2                  | 18-07-1991          |
|   |    |                     | AU | 8029187 A                  | 25-05-1988          |
|   |    |                     | DE | 3751348 D1                 | 20-07-1995          |
|   |    |                     | DE | 3751348 T2                 | 04-01-1996          |
|   |    |                     | EP | 0288570 A1                 | 02-11-1988          |
|   |    |                     | WO | 8803310 A1                 | 05-05-1988          |